

Metal Complexes of Functional Isocyanides, XXV^[◇]

Amino(hydrazino)carbene Complexes

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Received December 5, 1994

Key Words: *N*-Isocyanides / *N*-Isocyanodialkylamine complexes / Carbene complexes / Imaging-Plate data collection

The *N*-isocyanodialkylamine metal complexes $[M(CO)_5CN-NR_2]$ ($M = Cr, W$), *trans*- $[M_2(CNNR_2)_2]$ ($M = Pd, Pt$), *trans*- $[Pt(Cl)(CNNR_2)(PPh_3)_2]BF_4$, and *cis*- $[PtCl_2(CNNR_2)(PPh_3)]$ [$R = Et, iPr$; $2 R = -[CHMe(CH_2)_3CHMe]-$] react with primary amines to give the amino(hydrazino)carbene metal complexes $[M(CO)_5\{C(NHR')NHNHNR_2\}]$ ($R' = Me, nPr, Cy$) (**1–9**), *trans*- $[Pt_2\{C(NHMe)NHNHNR_2\}_2]$ (**10–12**) and *trans*- $[Pt(Cl)-\{C(NHMe)NHNHNC(H)(Me)(CH_2)_3CHMe\}(PPh_3)_2]BF_4$ (**13**), and the amine adducts *cis*- $[PtCl_2\{C(NHMe)NHNHNC(H)(Me)(CH_2)_3CHMe\}(PPh_3)] \cdot H_2NMe$ (**14**), and *trans*- $[PdI_2\{C(NHMe)NHNHNC(H)(Me)(CH_2)_3CHMe\}_2] \cdot 2 H_2NMe$ (**15**). With

secondary amines the amino(hydrazino)carbene metal complexes *trans*- $[PtCl\{C(NMe_2)NHNHNC(H)(Me)(CH_2)_3CHMe\}(PPh_3)_2]BF_4 \cdot HNMe_2$ (**18**) and *trans*- $[PtCl\{C(NEt_2)NHNHNC(H)(Me)(CH_2)_3CHMe\}(PPh_3)_2]BF_4$ (**19**) were isolated. The complexes *trans*- $[PtI_2\{C(NHCy)NHNHPr_2\}C(NHPr_2)]$ (**20**) and *trans*- $[PdI_2\{C(NHCy)NHNHPr_2\}_2]$ (**21**) were obtained by reaction of *trans*- $[M_2(CNNiPr_2)_2]$ ($M = Pd, Pt$) with cyclohexylamine. The structures were assigned on the basis of IR, NMR- (¹H, ¹³C, ³¹P), and mass spectroscopy as well as an X-ray structural analysis of **21**.

In 1969 Badley, Chatt and Richards^[2] found that coordinated isocyanides are converted into diheteroatom- and complex-stabilized carbenes by addition of nucleophiles such as alcohols or amines. In the course of our studies of the organometallic chemistry of *N*-isocyanides^[3,4], the question was raised as to whether this main reaction of *C*-isocyanides also applies here. We have recently reported on reactions of complexes of Bredereck's *N*-isocyanodialkylamines^[5] with secondary amines^[1]. Not unexpectedly, in these reactions cleavage of the N–N bond, presumably via an intermediate amino(hydrazino)carbene species, occurred with formation of cyanamide complexes. Alkyl- and aryl-(hydrazino)carbene complexes of chromium(0) had already earlier been postulated as unstable intermediates in the reaction of the corresponding alkoxy-carbene complexes with hydrazines. There, the product of the spontaneous N–N cleavage was a complex-bound nitrile^[6a,b]. More recent studies on the same subject are described in refs.^[6c,d]. In this context, the straightforward formation of isocyanato ($[M]-N=C=O$) complexes from metal carbonyls and hydrazine or azide, which also involves N–N cleavage, of intermediate carb(ox)hydrazido or carb(ox)azido complexes, deserves mentioning^[7,8].

Surprisingly, the same *N*-isocyanodialkylamine derivatives of the metal carbonyl reacted with primary amines to give the first stable and sometimes even sublimable pentacarbonyl[amino(hydrazino)carbene]chromium(0) and -tungsten(0) complexes^[9]. These complexes and analogous palladium(II) and platinum(II) products are described here^[10].

Results and Discussion

1. Syntheses of Amino(hydrazino)carbene Complexes

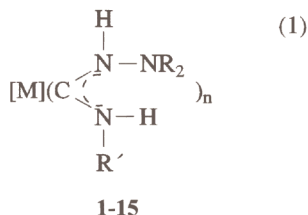
All of the studied *N*-isocyanodialkylamine complexes react rapidly with primary amines to afford amino(hydrazino)carbene complexes in good yields (eq. 1). The hexacarbonyl derivatives **1–9** are light yellow crystalline compounds some of which can be sublimed with little or no decomposition. Among the halogenopalladium and -platinum complexes the diiodoplatinum species **10–12** which readily crystallize possess the highest thermal stabilities (Table 4).

The IR spectra of all products show two $\nu(NH)$ bands in the range of 3400–3200 cm^{-1} and a strong broad band at 1570–1540 cm^{-1} , presumably representing the $\nu_{as}(N\equiv C\equiv N)$ mode superimposed by $\delta(>NH)$ vibrations.

[◇] Part XXIV: Ref. [1].

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The weak absorption at 1290–1260 cm⁻¹ is assigned to the symmetrical N=C=N stretching vibration (Table 1).



	[M]	R'	2 R	n
1	(CO) ₅ Cr	Me	2 <i>i</i> Pr	1
2	(CO) ₅ Cr	Me	-{MeCH(CH ₂) ₃ CHMe}-	1
3	(CO) ₅ Cr	Cy	-{MeCH(CH ₂) ₃ CHMe}-	1
4	(CO) ₅ W	Me	2 Et	1
5	(CO) ₅ W	Me	2 <i>i</i> Pr	1
6	(CO) ₅ W	Me	-{MeCH(CH ₂) ₃ CHMe}-	1
7	(CO) ₅ W	<i>n</i> Pr	2 <i>i</i> Pr	1
8	(CO) ₅ W	<i>n</i> Pr	-{MeCH(CH ₂) ₃ CHMe}-	1
9	(CO) ₅ W	Cy	-{MeCH(CH ₂) ₃ CHMe}-	1
10	I ₂ Pt[a]	Me	2 Et	2
11	I ₂ Pt[a]	Me	2 <i>i</i> Pr	2
12	I ₂ Pt[a]	Me	-{MeCH(CH ₂) ₃ CHMe}-	2
13 [c]	(PPh ₃) ₂ (Cl)Pt[a]	Me	-{MeCH(CH ₂) ₃ CHMe}-	1
14 [d]	(PPh ₃)Cl ₂ Pt[b]	Me	-{MeCH(CH ₂) ₃ CHMe}-	1
15 [d]	I ₂ Pd[a]	Me	-{MeCH(CH ₂) ₃ CHMe}-	2

[a] *trans*.- [b] *cis*.- [c] BF₄ salt.- [d] Methylamine adduct.

It was surprising that pentacarbonyl(*N*-isocyanide) complexes of chromium and tungsten undergo these reactions, even though we had shown earlier that pentacarbonyl(*N*-isocyanimine)tungsten(0) complexes form the corresponding amino(hydrazono)carbene species with amines^[11]. However, *C*-isocyanides bound in pentacarbonyl complexes do *not* react under the same conditions, while stronger nucleophiles such as organolithium reagents, exclusively attack a (*cis*-positioned) carbon monoxide ligand giving rise to carbene complexes of the Fischer type^[12]. Thus, the following order of reactivity towards nucleophiles is established:



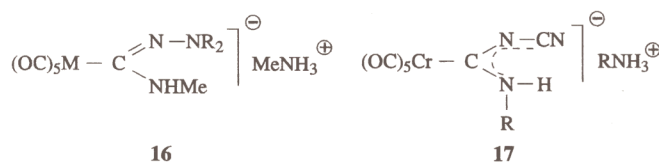
When the syntheses of **1**, **2**, and **4–6** were performed in liquid methylamine as solvent, a small amount of a white water-soluble byproduct remained after removal of the solvent and extraction of the neutral main product. The analytical and IR spectroscopic data of this byproduct point to a salt-like complex **16**. Deprotonation of the primary adduct to give **17** was also observed in the reaction of [Cr(CO)₅CNCN] with diisopropylamine, though in this case the equilibrium was completely shifted to the side of the ionic product^[13].

According to the analytical data, **14** and **15** exist as methylamine-rich products, though it is still not understood at the moment in which way the additional molecules of methylamine are bound in the complex. Still, bonding by hydrogen bridges to the amino(hydrazino)carbene ligands appears more plausible in these cases than a salt-like structure. This view is supported by an elemental analysis revealing

Table 1. Characteristic IR data [cm⁻¹] of the carbene complexes **1–21** (KBr)

	ν(NH)	ν(CH)	ν _{as/s} (N=C=N)	ν(CO) / Others
1	3380m, 3269m	2976m, 2936w, 2875w, 2840vw	1539s, 1261w	2053m, 1964m, 1932s, 1901vs, 1873vs
2	3364m, 3278m	2998vw, 2977w, 2967w, 2934m, 2864vw, 2850vw	1538s, 1269w	2055m, 1935sh, 1900vs, 1878vs
3	3333m, 3282m	2967sh, 2924m, 2851w	1553m, 1260w	2065w, 1971w, 1924s, 1892vs, 1868vs, 1593m δ(NH),
4	3363m, 3282m	2982m, 2940m, 2872w, 2849w,	1530s, 1269w	2065m, 1963m, 1888vs, 1871vs
5	3388m, 3292m, 3270w	2976m, 2935w, 2872vw	1544s, 1273w	2062m, 1903vs
6	3360m, 3287m	2977w, 2964w, 2940m, 2862w, 2848w, 2827w	1539s, 1272w-m	2062m, 1964m, 1891vs, 1868vs
7	3364m, 3276m	2974m, 2939m, 2875w, 2848w	1535m, 1262w	2061m, 1975m, 1939sh, 1912vs, 1864vs
8	3368m, 3267m	2876w, 2964w, 2941m, 2865w, 2850w	1533m, 1263w	2062m, 1974m, 1914vs, 1862vs
9	3423m, 3408m	2932s, 2905sh, 2856m	1563s	2068m, ca. 1922b,vs, 1853vs, 1604s δ(NH)
10	3319w, 3170w	2961w, 2927m, 2848w,	1552s, 1261w	
11	3310m, 3188m	2979s, 2947m, 2916m, 2865m	1558s, 1261w	
12	3305s, 3192m	2982m, 2953m, 2923s, 2855m	1563m, 1265w	
13	3320m, 3284sh	3056w, 2986sh, 2960sh, 2936s, 2858w	1580vs	1060vs ν(BF ₄)
14	3230s, br.	3050w, 2980w, 2962w, 2930s, 2858w	1571vs, 1290sh	1617s δ(NH)
15	3300sh, 3200s, br.	2985sh, 2962m, 2931s, 2854w-m	1569vs	
18	3290vw, sh	3050vw, 2924w	1559m	1055vs, br. ν(BF ₄)
19	3288w	3052w, 2963w, 2929m, 2864w	1573s, 1261w	1081s, br. ν(BF ₄) 309w. ν(PtCl)
20	3367w, 3255m	2973m, 2927s, 2852w	1563vs, 1260w	2187w ν(CN)
21	3320sh, 3269m, 3237m, 3200sh	2967m, 2925s, 2848m	1557vs, 1273w	

the presence in the monocarbene complex **14** of one, in the bis(carbene)palladium complex **15** however of two additional molecules of MeNH₂, i.e. one per each carbene ligand.



Due to the partial double bonds between the carbene carbon atom and the nitrogen neighbours, the amino(hydrazino)carbene ligands can occur in four different conformations of which, however, the *endolendo* and *exol* forms are rather unlikely to be verified^[14]. In the ¹H-NMR spectrum of pentacarbonyl{[(2,6-dimethylpiperidino)amino](methylamino)carbene}tungsten(0) (**6**), the assignment is relatively straightforward: A singlet at δ = 8.24 for the proton of the hydrazine substituent and a quadruplet at δ = 8.16 for the amine proton which may result (and thus

be assigned) from coupling with the *N*-methyl group ($^3J = 6$ Hz) appearing as a doublet at $\delta = 3.04$, suggest the presence of only one isomer as does the *one* methyl doublet of the 2,6-dimethylpiperidino group (Table 2). At first sight, the situation seems to be completely different in pentacarbonyl[(2,2-diisopropylhydrazino)(methylamino)carbene]chromium(0) (**1**): Here, *two* doublets are observed for the methyl protons of the isopropyl group, the ^{13}C -NMR spectrum also exhibiting *two* resonances for the methyl carbon atoms of the same group. Still, the nearly equal intensities of the doubled signals as well as the doublet at $\delta = 3.14$ (NHMe) and the singlet at $\delta = 6.04$ (NHNR₂) are inconsistent with the assumption of the presence of two *exolendo* isomers. Again it is suggested instead that only one isomer is present, however with a hindered rotation about the N–N bond for sterical reasons. In the case of the platinum complex **11** with its two presumably *trans*-positioned carbene ligands, an unambiguous assignment is no longer possible. In addition to the six NH resonances between $\delta = 8.62$ and 7.22, the spectrum shows several NCH₃ doublets superimposed by CH multiplets of the isopropyl groups ($\delta = 3.04$ –3.26). Their methyl protons again give rise to superimposing doublets. Similar findings have been reported for percarbeneplatinum complexes^[15] and the purely organic *N,N'*-dimethylacetamidium ion^[16]. The ^{13}C -NMR spectra of the pentacarbonyl(carbene)metal-6 complexes exhibit three low-field signals; in the case of the tungsten compounds, the most intense one is accompanied by ^{183}W satellites and assigned to the *cis*-CO ligands. It remains open, however, which of the two weaker signals originates from the carbene carbon atom and which from the *trans*-CO ligand. In the spectra of the platinum compounds **11** and **12** (as in the corresponding ^1H -NMR spectra) signals of several carbene species of different concentration are observed, none of which shows any platinum satellites however (Table 2).

The mass spectra of the amino(hydrazino)carbene derivatives of the hexacarbonyls (Table 3) are dominated by the typical loss of CO. The further degradation which runs parallel to the fragmentation of alkyl(amino)carbene complexes^[17] is illustrated in Scheme 1. As with the *N*-isocyanodialkylamine complexes, the main fragmentation process involves cleavage of the N–N bond with the formation of a free or complex-bound Schiff base^[3]. In the mass spectra of the platinum complexes, fragments of Schiff bases are insignificant (see Experimental).

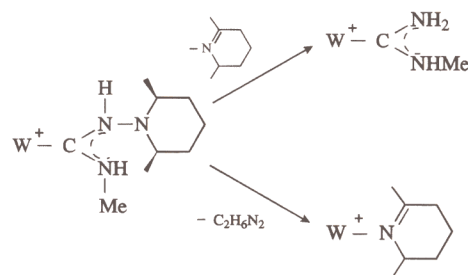
The reactions of the cationic complexes *trans*-[Pt(Cl)-{C[NHCHMe(CH₂)₃CHMe](PPh₃)₂]BF₄ and *trans*-[Pt(Cl)-(CNNEt₂)(PPh₃)₂]BF₄ with the *secondary* amines HNMe₂ or HNEt₂ afford the (dialkylamino)(2,2-dialkylhydrazino)carbene complexes **18** and **19**; this is in contrast to the corresponding reactions of hexacarbonyl derivatives and neutral platinum compounds which gave cyanamide and guanidine complexes, respectively^[11].

Compounds **18** and **19** were characterized on the basis of spectroscopic and analytical data (Tables 1, 2, 4). Thus, the ^1H -NMR spectrum of **19** exhibits an NH signal at $\delta = 9.42$. The multiplet at $\delta = 3.46$, formed by the superposition

Table 2. ^1H - and $^{13}\text{C}\{^1\text{H}\}$ -NMR data of selected compounds (δ values)

	^1H NMR	^{13}C NMR
1[a]	8.08 (NHMe, br., 1H), 6.04 (NH, s, 1H), 3.14 (NMe, d, 3H), 3.04 (CH, sept, 2H), 1.00 (CHMe, dd, 12H)	221.7, 220.2 (CO _{trans} , C _{carb}), 218.3 (CO _{cis}), 51.8 (CH), 34.2 (NMe), 20.8 (CHMe), 16.6 (CHMe)
6[b]	8.24 (NH, s, 1H), 8.16 (NHMe, q, 1H), 3.04 (NMe, d, 3H), 2.56 (CH, m, 2H), 1.60 (CH ₂ , m, 4H), 1.28 (CH ₂ , m, 2H), 0.88 (Me, d, 6H)	202.7, 199.6 (CO _{trans} , C _{carb}), 198.7 (s + ^{183}W satellites, CO _{cis} ; $^1J_{\text{WC}} = 126$ Hz), 58.5 (CH), 36.0 (NMe), 33.4 (CH ₂), 23.6 (CH ₂), 20.0 (CHMe)
8[b]	8.32 (NH, s, 1H), 8.16 (NHCH ₂ , t, 1H), 3.08 (NCH ₂ , m, 2H), 2.62 (CH, m, 2H), 1.66 (CHCH ₂ , m, 4H), 1.46 (CH ₂ Me, sext, 2H), 1.20 (CH ₂ , m, 2H), 0.90 (CHMe, d, 6H), 0.84 (CH ₂ Me, t, 3H)	202.4, 199.4 (CO _{trans} , C _{carb}), 198.7 (s + ^{183}W satellites, CO _{cis} ; $^1J_{\text{WC}} = 113$ Hz), 58.5 (CH), 50.9 (NCH ₂), 33.5 (CHCH ₂), 24.1 (CH ₂ Me), 23.5 (CH ₂), 19.6 (Me), 10.8 (CH ₂ Me)
11[b]	8.62 (s), 8.48 (s), 8.26 (dq), 7.62 (q), 7.22 (br.) (NH, 4H), 3.04–3.26 (CH, NMe, m, 10H), 0.86–1.16 (Me, m, 24H)	189.8, 188.3, 187.5, 186.4 (C _{carb}), 52.3, 51.7, 51.4, 51.2 (CH), 34.8, 34.6, 33.7 (NMe), 21.1, 21.0, 20.9, 20.6 (CHMe), 18.7, 18.3, 18.0, 17.7, 17.4, 16.9 (CHMe)
12[b]	8.78 (s), 8.49 (s), 8.28–8.06 (m), 7.72 (s), 7.50–7.22 (m) (NH, 4H), 3.08 (NMe, m, 6H), 2.50 (CH, m, 4H), 1.64 (CH ₂ , m, 8H), 1.18 (CH ₂ , m, 4H), 1.08–0.86 (Me, m, 12H)	188.4, 187.7, 184.1 (C _{carb}), 62.0, 60.6, 59.5, (CH), 35.0, 34.9, 34.1 (NMe), 31.8 (CH ₂), 23.6, 23.4 (CH ₂), 20.8, 20.5, 20.3, 20.1 (Me)
19[b]	9.42 (NH, s, 1H), 7.2–7.65 (PhH, m, 30H), 3.3–3.6 (CNCH ₂ , m, 4H), 1.54 (CH ₂ , q, 4H), 1.1–1.3 (CNCH ₂ CH ₃ , m, 6H), 0.50 (Me, t, 6H)	172.1 (C _{carb}), 134.5, 131.4, 129.4, 128.6 (C _{Ph}), 44.7 (CH ₂), 43.1 (CH ₂), 41.8 (CH ₂), 11.2 (Me), 10.4 (Me), 9.9 (Me)
21[a]	6.96 (NH, d, 1H), 6.44 (NNH, s, 1H), 4.46 (CH _{Cy} , m, 1H), 3.00 (CH, CH _{Cy} , m, 3H), 2.24–1.06 (m, 34H)	177.8 (C _{carb}), 57.3 (CNHCH), 53.4 (NH ₂ C), 52.9 (CH), 36.2, 32.5, 25.3, 25.2, 24.8, 21.1 (C _{Cy}), 17.7 (Me)

[a] Solvent CDCl₃, int. standard CHCl₃. – [b] Solvent [D₆]DMSO, int. standard TMS.

Scheme 1. Main fragmentation processes of pentacarbonyl[amino(hydrazino)carbene] complexes **1–9**

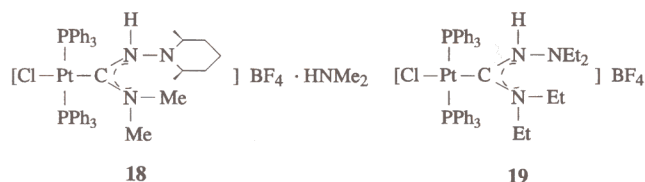
of several quartets, is assigned to the methylene protons of the amine part due to its low-field shift, whereas the multiplet at $\delta = 1.5$ is ascribed to the methylene protons of the hydrazino substituent. Since the methyl groups of the hydrazine part give rise to only *one* triplet at $\delta = 0.50$ it is assumed that only one isomer is present. The ^{13}C -NMR spectrum displays all the signals required by the three different types of ethyl groups; the ^{31}P -NMR confirms the *trans* position of the phosphane ligands. The molar mass

Table 3. Mass spectra [m/z (%)] of pentacarbonyl[amino(hydrazino)-carbene] complexes 1–9

Ion	1	2	3	6	8	9
$[\text{M}(\text{CO})_5\text{L}]^+$	349(14)	361(9)	429(9)	493(75)	521(68)	561(55)
$[\text{M}(\text{CO})_4\text{L}]^+$				465(7)	493(77)	533(36)
$[\text{M}(\text{CO})_3\text{L}]^+$	293(5)	305(3)	373(7)	437(80)	465(99)	505(78)
$[\text{M}(\text{CO})_2\text{L}]^+$	265(7)	277(5)	345(12)	407(37) ^[a]	435(29) ^[a]	475(19) ^[a]
$[\text{M}(\text{CO})\text{L}]^+$	237(19)	249(18)	317(22)	377(23) ^[b]	405(20) ^[b]	445(22) ^[b]
$[\text{ML}]^+$	209(100)	231(100)	289(100)	349(100) ^[b]	377(100) ^[b]	417(100) ^[b]
$[\text{MNR}_2\text{-H}]^+$	151(6)	163(12)	163(13)	283(69)	295(25)	295(17)
$[\text{ML-NR}_2\text{+H}]^+$	110(10)	110(19)	178(18)	242(28)	270(14)	310(13)

^[a] Additional loss of 2H. – ^[b] Additional loss of 4H.

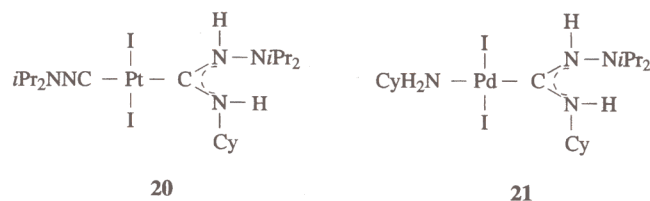
of the cation is inferred from the positive FAB spectrum (see Experimental).



2. Carbene/Isocyanide and Amine/Carbene Complexes

The reactions of *trans*-diiodobis(*N*-isocyanodiisopropylamine)platinum(II) and -palladium(II) with two equivalents of cyclohexylamine do not furnish the expected dicarbene complexes. In the case of $[\text{PtI}_2(\text{CNNiPr}_2)_2]$, after completion of the reaction, a band remains in the CN triple bond region which does not disappear even on addition of excess amine. The analytical and spectroscopic data are in accord with the formulation of a mixed carbene/isocyanide complex – *trans*- $[\text{PtI}_2\{\text{C}(\text{NHCy})\text{NHNiPr}_2\}(\text{CNNiPr}_2)]$ (**20**). Incomplete reaction with amines of (*tert*-butyl isocyanide)palladium complexes (however not of analogous platinum species) was also observed by Michelin et al. who attributed this behaviour to sterical effects^[18]. However, electronic effects must also be taken into account. From comparative studies of the bonding situation in isocyanide and carbene complexes, it was inferred that carbenes are considerably stronger σ donors^[19–21]. It is thus very obvious that the increased electron density at the metal atom resulting from the addition of amine to one isocyanide ligand renders any further nucleophilic attack at the remaining isocyanide ligand more difficult. Similar observations were made in our group for the attempted synthesis of carbene complexes from cyclohexyl isocyanide at palladium(II) and platinum(II): Instead of the desired homoleptic percarbene complexes, we could isolate only heteroleptic ones

which, however, underwent further reaction with a large excess of the amine or with a stronger nucleophile^[15].



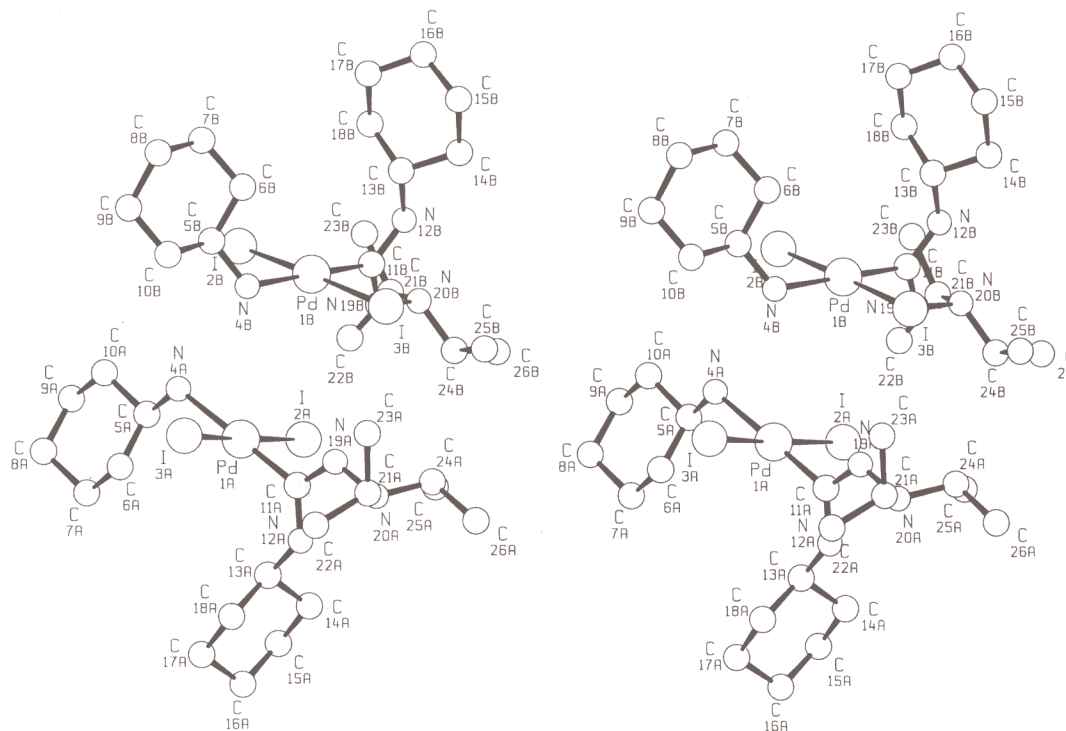
In the present example, the cyclohexyl substituent is introduced together with the amine component; the resulting carbenes hence contain the same electron-releasing alkyl group. A mixed isocyanide/carbene complex containing cyclohexyl groups – *trans*- $[\text{Pt}\{\text{Mo}(\text{CO})_3\text{-}\eta^5\text{-C}_5\text{H}_5\}_2(\text{CNCy})\{\text{C}(\text{OEt})\text{NHCy}\}]$ – was confirmed by X-ray spectroscopy^[22].

Interestingly, the reaction of the X-ray structurally-assessed *trans*-diiodobis(*N*-isocyanodiisopropylamine)palladium(II) with cyclohexylamine furnished neither a dicarbene nor a carbene/isocyanide complex, but rather the amine/carbene complex *trans*- $[\text{PtI}_2(\text{NH}_2\text{Cy})\{\text{C}(\text{NHCy})\text{NHNiPr}_2\}]$ (**21**) in good yield. We can only speculate on the mode of formation of the latter complex. Two different routes may be postulated: Formation of a carbene/isocyanide complex with substitution of the isocyanide by excess amine or, formation of a carbene/cyanamide (guanidine) complex with subsequent displacement of the cyanamide(guanidine) ligand^[1]. Relaxation of steric tension in the metal periphery is obviously not the driving force in this process. Inspection of a model immediately makes clear that the spatial requirement of the NH_2Cy ligands is markedly higher than that of the displaced diisopropyl-substituted *N*-isocyanide with its nearly linear $[\text{M}]\text{-C-N-N}$ skeleton.

The spectroscopic data of compounds **20** and **21** are compiled in Tables 1 and 2.

3. Crystal and Molecular Structure of *trans*-(Cyclohexylamine)[(cyclohexylamino)(2,2-diisopropylhydrazino)carbene]diiodopalladium(II) (**21**)

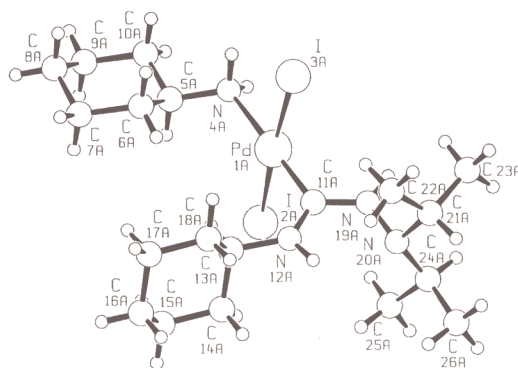
The crystal lattice of **21** is built up of pairs of crystallographically independent molecules **21A** and **21B** (Figure 1) which differ only slightly in their bonding parameters (Figure 2). The main difference obviously exists in the interplanar angles between the plane Pd, N4, C5 and the coordination plane about palladium. In terms of torsion angles along Pd–N4, these angles were determined as $-115.6(5)$ and $-58.4(5)^\circ$ for molecule A and B, respectively. Between the pairs no close contacts shorter than the sum of the corresponding van der Waals radii exist, and within the pairs, shortest intermolecular distances amount to 3.732 (I2A–N19B) and 3.885 Å (I2B–N4A); that is, we deal with very weak interactions; if any they are presumably hydrogen bonds. In spite of an almost stacked arrangement of the parallel coordination planes and the clearing away of the bulky cyclohexyl groups by outward rotations, that is,

Figure 1. Stereoplot of **21**

sterically favorable conditions for metal-metal bonds, the Pd...Pd distance of 4.341 Å precludes such interactions.

The pseudo-square planar coordination geometry around the central palladium is ideally realized by ligand–Pd–ligand' angles close to 90° and an exact planarity of the “best plane” through Pd, I2, I3, N4, and C11 (Figure 2, hydrogen atom positions calculated). All four Pd–I bond lengths [average value 2.654(3) Å] of the molecules **21A** and **21B** are identical and slightly elongated^[4] as compared with the starting complex *trans*-[PdI₂(C₄N₂H₆Pr₂)₂]: 2.590(1) Å. The Pd–C(carbene) bonds do not differ significantly either. They are, as in other doubly heteroatom-stabilized carbene-palladium complexes, for example, [Pd(C₄NHCH₂CH₂O)₄]Cl₂^[23] or [Pd(C₄NMeCH₂CHMeNH)₄]I₂^[15], only negligibly shorter than the sum of the covalent radii of Pd(II) (1.31 Å) and C_{sp²} (0.74 Å)^[24]. They possess single bond character.

It is well known that such carbene species do not generally require d_π–p_π back-bonding for their stabilization from any kind of metal^[25]. Rather, the electron deficiency at the carbene carbon atom is more than compensated by the p_π–p_π interactions with the neighbouring nitrogen atoms. This is reflected both by the consistently short C(carbene)–heteroatom bonds [here C–N: 1.344(8), 1.333(8) (**21A**) and 1.351(8), 1.322(8) (**21B**) Å] containing a considerable amount of double bond character, and by the hindered rotation around these bonds as well as by the planarity of the whole ligand. Important chemical consequences are the pronounced nucleophilicity of the complex-bound carbene carbon atom and – surprisingly – the relatively high stability of free carbenes of the imidazolin-2-ylidene type^[26].

Figure 2. SCHAKAL drawing of **21A**^[a]

^[a] Selected bond lengths [Å] and angles [°]: Pd–N4 2.164(6), Pd–C11 1.991(6), C11–N19 1.344(8), C11–N12 1.333(8), N19–N20 1.445(7); N4–Pd–C11 179.0(2), Pd–C11–N19 120.9(4), Pd–C11–N12 122.8(4), N19–C11–N12 116.3(5), C11–N19–N20 120.8(5).

The conformations in and about the *N,N'*-carbene ligand are also in full agreement with most of the results from stereochemical studies on such species obtained so far. Thus, the nearly perpendicular orientation of the carbene plane relative to the coordination plane of the d⁸ metal is typical and, although being attributed to only sterical reasons^[27] is usually retained^[28,29].

Likewise, the sterically more favorable “amphi” conformation of the nitrogen substituents, here with an *endo*-oriented diisopropylamino group (*E*) and an *exo*-oriented cyclohexyl group (*Z*)^[30], is also realized in all cases.

The N_(sp²)–N_(sp³) distance of 1.445(7) and 1.443(7) Å, respectively, corresponds to a normal N–N single bond^[31].

In view of an average Pd–N4 distance of 2.170(6) Å and the strong *trans* effect of the carbene ligand, the amine should be the most loosely bound and the most easily replaceable ligand so that its incorporation into the complex with substitution of the *N*-isocyanide [or even an amino(hydrazino)carbene ligand] is, strictly speaking, surprising. (Actually, a reaction path leading via a cyanamide, an excellent leaving. (Actually, a reaction path leading via a cyanamide, an excellent leaving group, would be most plausible, see above.)

Very suitable for comparison are the structures of chloro[3-(diethylamino)propionyl-*N,C*]((diethylamino)(methylamino)carbene)palladium(II), also crystallizing with two crystallographically independent molecules which contains an even longer bond [2.175(4), 2.181(5) Å] between the metal and a chelating amine *trans* to carbene^[32], and of [3-(dimethylamino)-1-(diphenylphosphanyl)propane-*N,P*] (isothiocyanato)(thiocyanato)palladium(II) exhibiting a Pd–N distance of 2.148(7) Å again to a chelating amine located in *trans* position with respect to the *S*-bound thiocyanate^[33].

In view of the relatively large orthorhombic cell of **21** with a volume of more than 11000 Å³ (Table 5) and the resolution of $\sin\Theta/\lambda \approx 0.6 \text{ Å}^{-1}$ usually required (corresponding to a Cu-limiting sphere), we were confronted with the problem of measuring the intensities of about 10000 independent reflections, which in the case of a conventional diffractometer equipped with a scintillation counter would have been a very time-consuming process. Another problem would have been the selection of the primary radiation. Cu radiation had to be ruled out because of its high absorption, while with Mo radiation using a counter diffractometer, there was the risk of an overlapping of adjacent reflections due to the large lattice constant *a* of more than 35 Å. Compound **21** therefore appeared to be a good candidate for a test of the new imaging-plate system for the solution of structural problems in inorganic and organometallic chemistry. The method has so far found application mainly in protein crystallography.

In total, 80699 reflections were measured with an imaging-plate scanner from Mar Research using Mo-*K*_α radiation (graphite monochromator). The total measurement was performed in less than 12 hours. After averaging over symmetry-equivalent reflections with the program DENZO^[34], 9209 independent reflections (*R*_{int} = 0.04) were obtained, corresponding to 88.5% of all attainable reflections in the range $\sin\Theta/\lambda \leq 0.6 \text{ Å}^{-1}$.

The subsequent structure determination with SHELXS^[35] and the refinement with XTAL^[36] were carried out without any problems. The final *R* values of *R* = 0.046 and *R*_w = 0.041 showed that a data set was obtained the precision of which may presumably not even be improved by means of a counter diffractometer. On the other hand, the imaging-plate method is clearly superior to the use of conventional diffractometer because it is much faster. Also, the previously mentioned problem of overlapping of adjacent reflections proved to be irrelevant in spite of a lattice constant of about 35 Å. Thus, the application of the imag-

ing-plate method for the structure determination discussed in this paper has proven advantageous in every respect. Efforts should therefore be made to use this method not only in protein crystallography but to a larger extent also in other fields^[37].

We are indebted to the *Deutsche Forschungsgemeinschaft*, the *Fonds der Chemischen Industrie* and the *BMBW (Graduiertenkolleg "Synthesis and Structure of Low Molecular Compounds")* for their generous financial support.

Experimental

All experiments were performed under argon in dried argon-saturated solvents. The *N*-isocyanide complexes [M(CO)₅CNNR₂] (M = Cr, W) and *trans*-[MI₂(CNNR₂)₂] (M = Pd, Pt), *trans*-[Pt(Cl)(CNNR₂)(PPh₃)₂]BF₄, *cis*-[PtCl₂(CNNR₂)(PPh₃)] (R = Et, *i*Pr; 2 R = –{MeCH(CH₂)₃CHMe}–) were prepared according to literature procedures^[3,4]. – IR: Beckman IR 4220 and Perkin-Elmer 983. – NMR: Bruker AM 270. – MS: Varian CH5 and

Table 4. Analytical data, melting points, and yields of **1–21**

	Empirical formula (mol. mass)	Color	Analyses data		found	m. p. (dec.) [°C]	Yield [%]
			%C	%H	calcd. %N		
1	C ₁₃ H ₁₉ CrN ₃ O ₅ (349.31)	light- yellow	44.47 44.70	5.61 5.48	12.19 12.03	62	86
2	C ₁₄ H ₁₉ CrN ₃ O ₅ (361.16)	light- yellow	46.67 46.54	5.22 5.30	11.60 11.63	140	ca.90
3	C ₁₉ H ₂₇ CrN ₃ O ₅ (429.44)	light- yellow	53.37 53.14	6.56 6.34	10.11 9.78	73	78
4	C ₁₁ H ₁₅ N ₃ O ₅ W (453.11)	light- yellow	31.01 29.16	3.44 3.34	9.79 9.27	122	ca.90
5	C ₁₃ H ₁₉ N ₃ O ₅ W (481.16)	light- yellow	32.69 32.45	3.94 3.98	8.85 8.73	89-91	ca.90
6	C ₁₄ H ₁₉ N ₃ O ₅ W (493.17)	light- yellow	34.11 34.10	3.94 3.88	8.85 8.52	172	ca.90
7	C ₁₅ H ₂₃ N ₃ O ₅ W (509.21)	light- yellow	35.67 35.38	4.39 4.55	8.12 8.25	152	ca.90
8	C ₁₆ H ₂₃ N ₃ O ₅ W (521.29)	light- yellow	37.10 36.87	4.67 4.45	8.19 8.08	132	87
9	C ₁₉ H ₂₇ N ₃ O ₅ W (561.29)	light- yellow	41.79 40.66	4.56 4.85	7.59 7.49	180	92
10	C ₁₂ H ₃₀ I ₂ N ₆ Pt (707.30)	light- yellow	21.01 20.38	4.37 4.28	11.31 11.88	188	88
11	C ₁₆ H ₃₈ I ₂ N ₆ Pt (763.41)	light- yellow	24.94 25.17	4.93 5.02	11.21 11.01	180	93
12	C ₁₈ H ₃₈ I ₂ N ₆ Pt (787.43)	light- yellow	27.18 27.46	4.84 4.86	10.44 10.67	194	86
13	C ₄₅ H ₄₉ BClF ₄ N ₃ P ₂ Pt (1011.19)	colorless	52.30 53.45	4.56 4.88	4.14 4.16	[a]	ca.70
14	C ₂₇ H ₃₉ N ₄ Cl ₂ Pt (728.60)	white- grey	44.87 46.16	5.54 5.40	7.67 7.69	[a]	ca.70
15	C ₂₀ H ₄₈ I ₂ N ₈ Pd (760.88)	light - ockre	30.79 31.57	6.29 6.36	14.68 14.73	[a]	ca.70
18	C ₄₈ H ₅₈ BClF ₄ N ₄ P ₂ Pt (1070.30)	colorless	53.46 53.87	4.91 5.46	5.27 5.23	[a]	ca.70
19	C ₄₅ H ₅₁ BClF ₄ N ₃ P ₂ Pt (1013.20)	colorless	52.92 53.35	4.56 5.07	4.63 4.15	177	85
20	C ₂₀ H ₄₁ I ₂ N ₅ Pt (800.47)	yellow	29.63 30.01	5.44 5.16	8.97 8.75	168	62
21	C ₁₉ H ₄₀ I ₂ N ₄ Pd (684.78)	orange	33.63 33.33	5.20 5.89	8.12 8.18	156	72

[a] Not determined.

Finnigan Mat 711 (excitation energy 80 eV each). — Elementary analyses: CHN Rapid. — Melting and decomposition points (uncorrected): Melting point apparatus or Büchi modell 510 (Table 4).

1. *Pentacarbonyl[(2,2-dialkylhydrazino)(methylamino)carbene]chromium(0)* (**1**, **2**) and *-tungsten(0)* (**3**, **4**)

a) Approximately 250 mmol of the *N*-isocyanide complex was placed in a small Schlenk flask which was flushed with a weak stream of dry methylamine. The reaction vessel was subsequently cooled to -50°C , and ca. 10 ml of methylamine was condensed into the mixture until the complex had dissolved in the liquid phase. After the mixture had been stirred at -10°C for 2 h, it was slowly warmed to room temp., and excess methylamine was evaporated. The yellow raw product was dried in vacuo and extracted several times with petroleum ether. The combined extracts were concentrated and cooled to -78°C . The crystallized product was collected on a cooled frit and dried in high vacuum for several hours. Yields ca. 30–40%. After extraction, a small amount of a white salt-like substance remained, which was identified as complex **16**, $\text{M} = \text{Cr}$, $\text{R} = i\text{Pr}$. — IR (KBr): $\tilde{\nu} = 3406 \text{ w cm}^{-1}$ (NH), 3120–2763 m (NH, CH), 2052 m, 1920 vs, 1883 vs (CO). — $\text{C}_{14}\text{H}_{24}\text{CrN}_4\text{O}_5$ (380.4): calcd. C 44.21, H 6.36, N 14.73; found C 43.82, H 6.58, N 15.12.

b) Into a solution of 1.0 g of the *N*-isocyanide complex in 10 ml of *n*-pentane, ca. 5 ml of methylamine was condensed at -30°C . The mixture was stirred for 2 h and subsequently allowed to warm slowly to room temp. during which time it turned yellow-green. After evaporation of the solvent the residue was extracted with petroleum ether and the product crystallized at -78°C . Yields, analytical data, colors, and melting points are compiled in Table 4. The molar masses were determined by mass spectroscopy.

2. *Pentacarbonyl(alkylamino)(2,2-dialkylhydrazino)carbene]chromium(0)* (**3**) and *-tungsten(0)* (**7–9**): To a solution of 1.0 g of the *N*-isocyanide complex in 10 ml of pentane, an equimolar amount of the corresponding amine was added, and the mixture was stirred for 2 h. During this period it turned yellow-green. After evaporation of the solvent, the raw product was extracted with petroleum ether, the extract was concentrated, and the product frozen out at -78°C . It was subsequently dried in high vacuum for several hours.

3. *trans-Bis[(2,2-dialkylhydrazino)(methylamino)carbene]diiodoplatinum(II)* (**10–12**) and *trans-Chloro{[(2,6-dimethylpiperidino)amino](methylamino)carbene}bis(triphenylphosphane)platinum(II)* Tetrafluoroborate (**13**): To a solution of 1.0 g of the *N*-isocyanide complex in 10 ml of dichloromethane, 5 ml of methylamine at -30°C was condensed, and the mixture was stirred for 2 h. It was subsequently allowed to warm slowly to room temp., and the solvent was evaporated. The raw products were washed several times with ether, dried in high vacuum for several days and recrystallized from dichloromethane/petroleum ether. — **11**: MS, m/z (%): 763 (42) $[\text{M}^+]$, 636 (40) $[\text{M}^+ - \text{I}]$, 479 (9) $[\text{M}^+ - \text{I} - \text{L}]$; **12**: 787 (3) $[\text{M}^+]$, 660 (4) $[\text{M}^+ - \text{I}]$.

4. *cis-Dichloro{[(2,6-dimethylpiperidino)amino](methylamino)carbene}(triphenylphosphane)platinum(II)* (**14**) and *trans-Bis{[(2,6-dimethylpiperidino)amino](methylamino)carbene}diiodopalladium(II)* (**15**): The reactions were performed as described in 1a). The sticky raw products which remained after evaporation of methylamine were digested with ether thereby causing crystallization. The crystals were washed several times with ether and dried in vacuum for 1 d. The compounds crystallized with one (**14**) or two molecules of methylamine (**15**).

5. *trans-Chloro{[(dimethylamino)[(2,6-dimethylpiperidino)amino]carbene}bis(triphenylphosphane)platinum(II)* Tetrafluoroborate

Table 5. Crystal and measuring data of **21**

Empirical formula: $\text{C}_{19}\text{H}_{40}\text{I}_2\text{N}_4\text{Pd}$; mol. mass 684.78 g/mol; crystal habitus: orange-coloured needles; crystal size: $0.52 \times 0.16 \times 0.20 \text{ mm}$; space group: *Pbca*; $Z = 16$; $a = 35.30(2)$, $b = 13.80(2)$, $c = 23.10(2) \text{ Å}$; $V = 11253 \text{ Å}^3$; $d_{\text{calcd.}} = 1.615 \text{ Mg m}^{-3}$; $\mu(\text{Mo-K}\alpha) = 28.76 \text{ cm}^{-1}$; measuring range $3.62^{\circ} \leq 2\theta \leq 50.68^{\circ}$; scan-Mode: ω -scan; no absorption correction; total no. of reflections: 80699; no of independent reflections: 9209; 470 refined parameters; max. residual electron density: 2.319 e/Å^3 ; $R = 4.6\%$, $R_w = 4.1\%$

(**18**): Same procedure as described in 4. The compound crystallized with one molecule of dimethylamine.

6. *trans-Chloro[(diethylamino)(2,2-diethylhydrazino)carbene]bis(triphenylphosphane)platinum(II) Tetrafluoroborate* (**19**): To a solution of 1.0 g (1.06 mmol) of the *N*-isocyanide complex in dichloromethane, 0.1 g (1.37 mmol) of diethylamine was added, and the mixture was stirred for 5 h. After evaporation of the solvent in vacuo the residue was washed with ether and recrystallized from dichloromethane/*n*-hexane. — ^{31}P NMR (CH_2Cl_2 ; ext. standard H_3PO_4): $\delta = 17.8 \text{ (s, } ^{195}\text{Pt satellites, } ^1J_{\text{PtP}} = 1617 \text{ Hz)}$. — MS, m/z (%): 926 (17) $[\text{M}^+ - \text{BF}_4]$.

7. *trans-[(Cyclohexylamino)(2,2-diisopropylhydrazino)carbene]diisopropylhydrazonomethylene)diiodoplatinum(II)* (**20**): To a solution of 0.3 g (0.43 mmol) of the *N*-isocyanide complex in dichloromethane, 1.0 g (1.01 mmol) of cyclohexylamine was added, and the mixture was stirred for 2 d. After evaporation of the solvent in vacuo the residue was washed with ether and recrystallized from dichloromethane/*n*-hexane. — MS, m/z (%): 800 (13) $[\text{M}^+]$, 673 (28) $[\text{M}^+ - \text{I}]$, 545 (43) $[\text{M}^+ - \text{I} - \text{HI}]$.

8. *trans-(Cyclohexylamine)[(cyclohexylamino)(2,2-diisopropylhydrazino)carbene]diiodopalladium(II)* (**21**): Same procedure as in 7. — MS, m/z (%): 683 (3) $[\text{M}^+ - \text{H}]$, 557 (2) $[\text{M}^+ - \text{I}]$, 458 (3) $[\text{M}^+ - \text{I} - \text{L}']$, 330 (4) $[\text{M}^+ - \text{I} - \text{L}' - \text{HI}]$.

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